

TITLE: Water Gas Shift Kinetics at Membrane Reactor Conditions

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GRANT NUMBER: DE-FG2699-FT40590

PERIOD OF
PERFORMANCE: June 30, 1999 – June 29, 2002

DATE: April 16, 2002

ABSTRACT

The water-gas shift reaction converts CO and H₂O into CO₂ and H₂. In the processing of coal water-gas shift may be important either to shift the CO/H₂ ratio of the gasifier product prior to Fischer-Tropsch synthesis. Alternatively, if H₂ is the desired product, it may be used to increase H₂ yield while simultaneously generating CO₂ that can be sequestered underground or elsewhere. Water-gas shift is exothermic and reversible meaning that conversion is limited by thermodynamic equilibrium at higher temperatures while the rate of reaction is low at lower temperatures. Membrane reactor technology, if it can be economically developed, would eliminate this trade-off by separating the H₂ as it is produced. The objective of this project was to determine whether current commercial water-gas shift catalysts could be used effectively in a membrane reactor, and if they could not, to develop catalysts that were more suitable.

During the first two years of the award, a detailed mechanistic model was developed for the catalytic kinetics of water-gas shift over iron-chromium high temperature catalysts. This catalyst is inhibited by CO₂. This was shown to be detrimental to performance in a membrane reactor. The model predicted that if a promoter was found that would weaken the strength of the surface oxygen bonds, the resulting catalyst would be both more active and less susceptible to inhibition by CO₂. A review of the literature had revealed that a Ce promoter caused a shift of the temperature-programmed reduction (TPR) peak temperature to lower values. This might have been indicative of a weaker surface oxygen bond strength, but when a Ce-promoted catalyst was tested for water-gas shift, its performance was found to be virtually identical to the unpromoted catalyst. The foci of the research during this final year have been to determine whether the mechanistic model was wrong or whether there was a different cause for the shift

in the TPR peak temperature of the Ce-promoted catalyst and to continue to seek to develop water-gas shift catalysts that were better suited to membrane reactor use.

The Ce-promoted catalyst was examined via scanning electron microscopy, tested further for water-gas shift performance, and measured for specific surface area before and after reaction. The temperature-programmed reduction behavior was also examined. We now believe that the shift of the TPR peak temperature to lower values was associated with the reduction of a separate ceria component of the catalyst. Thus, this shift in peak temperature is NOT indicative of a reduction in the surface bond strength of the catalytically active iron-chrome oxide phase.

Another literature report (Kappen et al., *J. Catal.*, 2001) indicates that a Cu-promoted iron-chrome catalyst exhibits a similar shift of the TPR peak to lower temperatures relative to the unpromoted catalyst. When the water-gas shift was studied over this catalyst, we found that the degree of inhibition by CO₂ was less than that of an unpromoted catalyst. The effect of Cu promoter loading on the catalyst has been studied. The optimum loading appears to be of the order of 5 wt.%; additional Cu does not further increase the resistance to inhibition by CO₂. The kinetics of the reaction have additionally been studied at total pressures up to ca 100 psi over the Cu-promoted catalyst. The results are consistent with the predictions of the original mechanistic kinetic model for the iron-chrome catalyst. Consequently, the same mechanistic model has been fit to the data for the Cu-promoted catalyst. Transient experiments using a microbalance are currently underway. In these experiments we are attempting to measure changes in the amount of surface oxygen as reaction conditions are varied and compare the results to those predicted by the mechanistic model.

In a separate effort, we have performed a computational analysis of the performance of CoMo sulfide water-gas shift catalysts under membrane reactor conditions. Our kinetic modeling suggests that these catalysts are not inhibited by the presence of CO₂, and consequently they might perform very well in a membrane reactor. These materials might be quite useful for water-gas shift in a coal processing context because the sulfur native to the coal might be sufficient to maintain them in their active state. There are a few critical questions regarding these sulfur-tolerant water-gas shift catalysts that remain unanswered. The first is related to available membrane materials: can these catalysts maintain activity at the low sulfur concentrations where the membranes are not poisoned by the sulfur. The second is whether these catalysts can be operated at higher temperatures; they typically have been studied at temperatures that are lower than used with iron-chrome water-gas shift catalysts. The third is whether they are affected by the chemical form of the sulfur, e.g. H₂S vs. thiol, etc. These experimental issues have been proposed for study in a pending proposal.

In summary, the project has been very successful. It was shown that there are significant limitations to the use of existing iron-chrome high-temperature water-gas shift catalysts in membrane reactors. The mechanistic model for the kinetics of water-gas shift that was developed in this study was successfully used to guide the development of an improved, Cu-promoted catalyst. This mechanistic model can still serve in this manner, being used as a tool to suggest effective catalyst modifications leading to still-better catalysts. Additionally, sulfur-tolerant water-gas shift catalysts were identified as a class of catalysts that may function very well in a membrane reactor. Critical issues related to this use of sulfur-tolerant catalysts for water-gas shift in a membrane reactor have been identified.